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Electron Paramagnetic Resonance Studies of Cobalt (II) Thioiminato Schiff Base Compound with Lewis Bases and Its Oxygen Adducts

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EPR spectra were observed for N,N' -ethylenebismonothioacetylacetoneiminatocobalt (II), $\text{Co}(\text{sacac})_2\text{en}$, with the Lewis bases, LB, (pyridine, 4-methylpyridine, 4-cyanopyridine, piperidine, N -methylimidazole and N,N -dimethylformamide) and their oxygen complexes. The EPR spectra show that all of the $\text{Co}(\text{sacac})_2\text{en}(\text{LB})$ complexes have the rhombic symmetry with $(d_{x^2-y^2}, d_{xz}, d_{yz})^6-(d_z^2)^1$ ground configuration. Cobalt-59 hyperfine coupling constants are utilized in evaluating the unpaired electron spin distribution. The total cobalt spin densities are found to fall in the range of 0.66–0.78 and to be mainly localized on the cobalt atom for $\text{Co}(\text{sacac})_2\text{en}(\text{LB})$. $\text{Co}(\text{sacac})_2\text{en}(\text{LB})$ forms a monomeric 1 : 1 complex with molecular oxygen reversibly. It is found that the EPR parameters of the oxygen adducts are very similar for these Lewis bases.

INTRODUCTION

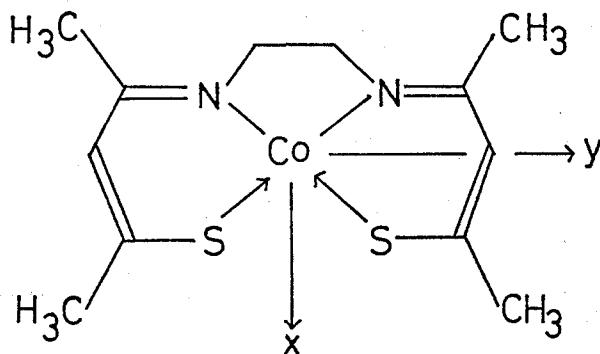
Low-spin cobalt (II) complexes with Schiff bases and porphyrins have recently received considerably interest because of their ability to form monomeric complexes with molecular oxygen reversibly.^{1~8)} Nitrogen donor adducts and their oxygenated complexes have been particularly investigated to understand the transport of molecular oxygen and oxidation by it in biological systems.^{6~8)} But little is known about the corresponding complexes with Schiff bases containing sulphur atom. It appears clearly that the behavior of the complexes containing sulphur atom is specific for the redox reaction from the recent studies of Ferredoxin and its related complexes.^{9~11)} Therefore, it is significant to study the role of sulphur atom for the electron transfer reaction; $\text{Co}(\text{II}) + \text{O}_2 = \text{Co}(\text{III})\text{O}_2^-$.

We report on EPR studies for N,N' -ethylenebismonothioacetylacetoneiminatocobalt (II), $\text{Co}(\text{sacac})_2\text{en}$, with nitrogen donors and discuss the results on the basis of the unpaired electron confined in a cobalt-nitrogen σ molecular orbital. Cobalt-59 hyperfine constants are used in evaluating the unpaired electron distribution. The reversible monomeric $\text{Co}(\text{sacac})_2\text{en}(\text{LB})\text{O}_2$ complexes are reported and found to have similar magnetic parameters for various axial ligands.

EXPERIMENTAL

Materials. *The synthesis of N,N' -ethylenebismonothioacetylacetoneimine, $H_2(\text{sacac})_2$*

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en. $\text{H}_2(\text{sacac})_2\text{en}$ was prepared by substitution of the oxygen atom of $\text{N,N}'$ -ethylenebis-acetylacetoneimine, $\text{H}_2(\text{acac})_2\text{en}$, to sulphur atom.¹²⁾ Triethyloxonium tetrafluoroborate, $(\text{Et}_3\text{O})^+(\text{BF}_4)^-$, (0.1 mol) dissolved in dichloromethane (50 ml) was added to a solution of $\text{H}_2(\text{acac})_2\text{en}$ (0.05 mol) in dichloromethane (100 ml) with stirring under an atmosphere of nitrogen. After addition was complete, the mixture was more stirred for an additional 30 min. At the end of this time, a fine suspension of excess NaHS in ethanol was added to mixture. This mixture was stirred for 60 min and filtered to remove the insoluble sodium tetrafluoroborate. The filtrate was evaporated to dryness *in vacuo* and the crude ligand was recrystallized from acetone-water. (Found: C, 55.94; H, 8.09; N, 10.79%. Calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{S}_2$: C, 56.20; H, 7.86; N, 10.93%.)

$\text{H}_2(\text{acac})_2\text{en}$ and $(\text{Et}_3\text{O})^+(\text{BF}_4)^-$ were prepared according to the literatures.^{13,14)}

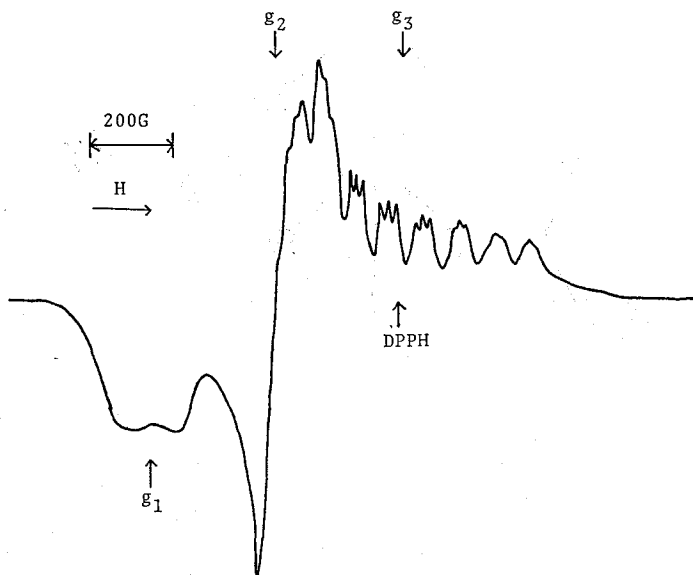
The synthesis of Co(sacac)₂en. This complex was prepared under an atmosphere of nitrogen. Cobalt acetate tetrahydrate (0.01 mol) and $\text{H}_2(\text{sacac})_2\text{en}$ (0.01 mol) were dissolved in methanol (100 ml). The solution was warmed for 30 min on a steam bath and then cooled overnight in the refrigerator. The complex was obtained as red crystals. (Found: C, 45.90; H, 6.06; N, 8.73%. Calcd for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{S}_2\text{Co}$: C, 46.00; H, 5.79; N, 8.94%.)

Pyridine, 4-methylpyridine, 4-cyanopyridine, piperidine, *N*-methylimidazole, and *N,N*-dimethylformamide were purchased commercially.

Measurements. The EPR spectra of the complex were measured in toluene containing a proper quantity of the Lewis base (LB) at 77 and 193 K. Prior to a measurement, each sample was degassed thoroughly. These samples could be oxygenated by exposure to oxygen gas *ca* -20°C more than 20 min.

RESULTS AND DISCUSSION

EPR spectra of Co(sacac)₂en with nitrogen donors. The EPR spectrum of $\text{Co(sacac)}_2\text{en}$ in 10% pyridine-toluene at 77 K is shown in Fig. 1. The spectrum has three components of *g*-factor, suggesting that the Co(II) ion is placed in a rhombic symmetry. For the high field, seven of the eight ^{59}Co ($I=7/2$) hyperfine lines are clearly resolved and several have seen to be splitted into equally intensified triplet by the single ^{14}N ($I=1$) of one axially coordinated pyridine molecule. A similar spectrum is observed in pyridine at 77 K. The samples with the other Lewis bases except *N,N*-dimethylformamide give

Fig. 1. EPR spectrum of $\text{Co(sacac)}_2\text{en(pyridine)}$ in frozen toluene solution at 77K.

quantitatively identical spectra. This suggests that $\text{Co(sacac)}_2\text{en}$ exists as a five coordinated complex, $\text{Co(sacac)}_2\text{en(LB)}$, in these solutions.

The associated EPR parameters are listed in Table I. In each complex the g values and cobalt hyperfine coupling constants are consisted with a $(d_x^2-y^2, d_{xz}, d_{yz})^6(d_z^2)^1$ ground configuration. The magnetic parameters for this ground configuration are

$$g_{xx} = 2.002 - 6\lambda/\Delta E_{yz \rightarrow z^2}$$

$$g_{yy} = 2.002 - 6\lambda/\Delta E_{xz \rightarrow z^2}$$

$$g_{zz} = 2.002$$

$$A_{xx} = P[-k - 2/7 + (g_{xx} - 2.002) + 1/14(g_{yy} - 2.002)]$$

$$A_{yy} = P[-k - 2/7 + (g_{yy} - 2.002) + 1/14(g_{xx} - 2.002)]$$

$$A_{zz} = P[-k + 4/7 + 1/14(2.002 - g_{xx} + 2.002 - g_{yy})]$$

where λ is the effective spin-orbit coupling constant in the complex.¹⁵⁾ ΔE values are the energy separations of between d_{xz} , d_{yz} , and d_z^2 , and Pk is the Fermi contact term.

Table I. EPR Parameters for $\text{Co(sacac)}_2\text{en(LB)}$ Complexes

LB	g_1	g_2	g_3	A_1	$-A_2$	A_3	A_3^N
pyridine	2.444	2.207	2.000	22.0	12.3	77.2	15.3
4-methylpyridine	2.421	2.05	2.004	12.4	18.6	70.8	15.0
4-cyanopyridine	2.431	2.223	1.996	20.6	11.8	82.0	14.9
N-methylimidazole	2.421	2.219	1.993	2.8	28.4	65.0	16.3
piperidine	2.432	2.189	2.004	14.6	17.4	67.1	7.5

A: 10^{-4} cm^{-1}

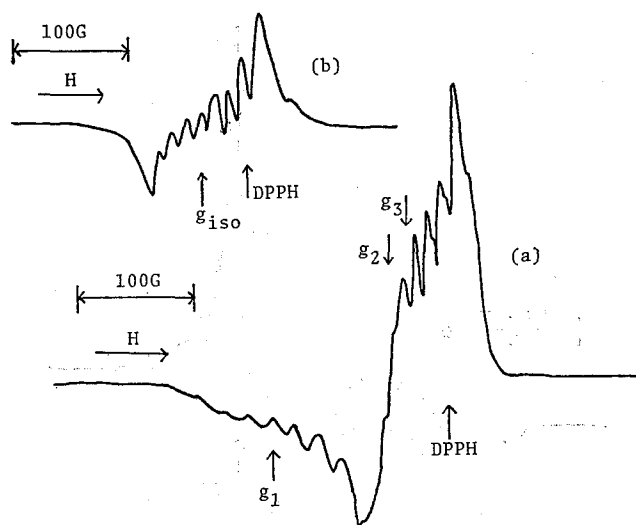
Table II. Cobalt-59 Spin Densities Calculated from EPR Parameters for Co(sacac)₂en(LB)

LB	P (cm ⁻¹) ^{a)}	k	-A _c ^{b)}	-A _d	ρ _{3d} ^{c)}	ρ _{4s}	ρ _{Co}
pyridine	0.0156	0.030	4.7	89.1	0.68	0.042	0.72
4-methylpyridine	0.0154	0.068	10.4	88.0	0.67	0.037	0.1
4-cyanopyridine	0.0168	0.036	6.1	96.0	0.73	0.045	0.78
N-methylimidazole	0.0165	0.132	21.7	94.3	0.72	0.031	0.75
piperidine	0.0142	0.055	7.8	81.1	0.62	0.036	0.66

A: 10⁻⁴ cm⁻¹a) P and k values are based upon a (d_{x²-y²}, d_{xz}, d_{yz})³(d_{z²})¹ ground configuration for cobalt (II).b) A_c and A_d are the cobalt-59 contact and dipolar hyperfine constants corrected for orbital magnetism (A_c = -Pk, A_d = 4/7P).c) ρ_{3d} and ρ_{4s} are the spin densities in the cobalt 3d and 4s orbitals estimated from cobalt hyperfine constants.

Second-order contribution is not significant for Co(sacac)₂en(LB) where $\Delta E_{xz \rightarrow z^2}, \Delta E_{yz \rightarrow z^2} \gg \lambda$. The electronic parameters that result from solving these expressions for nitrogen donors are given in Table II. Using the observed g_{xx} , g_{yy} and the d_{xz} , $d_{yz} \rightarrow d_{z^2}$ energy separations, an effective spin-orbit coupling constant reduced from the free Co(II) ion value ($\lambda_0 = -515$ cm⁻¹) is obtained. The cobalt P value reduced from the free ion value ($P_0 = 0.023$) permits the evaluation of the cobalt hyperfine constants, which is estimated according to the equation, $P = P_0 \lambda / \lambda_0$.¹⁰⁾ The reduction of the cobalt P value and the effective spin-orbit coupling constant from the free ion values is largely caused by the redistribution of the unpaired electron from the d_{z^2} to the σ donor orbital of the axial ligand.

Cobalt 3d_{z²} spin density (ρ_{3d}) is estimated from comparison of the observed dipolar coupling constant (A_d) with the theoretical value (A_d = 4/7P₀ = 0.01314 cm⁻¹) for a cobalt 3d electron. Cobalt 4s spin density (ρ_{4s}) is estimated from the Symons' equation

Fig. 2. EPR spectra of Co(sacac)₂en in toluene solution containing 10% pyridine and O₂ gas.

(a) 77 K (b) 193 K

Table III. EPR Parameters for $\text{Co}(\text{sacac})_2\text{en}(\text{LB})(\text{O}_2)$ Complexes

LB	g_1	g_2	g_3	g_{iso}	$-A_1$	$-A_2^{\text{a)}}$	$-A_3$	$-A_{\text{iso}}$
pyridine	2.086	2.013	2.002	2.026	19.1	7.5	11.3	12.6
4-methylpyridine	2.089	2.019	2.008	2.024	18.8	6.5	10.6	12.0
4-cyanopyridine	2.076	2.011	2.001	2.024	19.3	8.7	11.3	13.1
piperidine	2.080	2.023	2.015	2.026	18.5	11.3	11.7	13.8
N-methylimidazole	2.093	2.021	2.008	2.034	19.9	4.1	11.3	11.6
N,N-dimethylformamide	2.097	2.015	2.001	2.029	28.0	1.3	13.2	13.3

A: 10^{-4} cm^{-1} a) A_2 values are calculated from $A_2 = 3A_{\text{iso}} - (A_1 + A_3)$.

$$A_{\text{contact}} = -P_k = \rho_{4s}A(\text{Co}4s) + \rho_{3d}A(\text{Co}3d)$$

where $A(\text{Co}4s) = 0.1232 \text{ cm}^{-1}$ and $A(\text{Co}3d) = -0.00840 \text{ cm}^{-1}$.¹⁷⁾ The total cobalt spin density falls in the range 0.66~0.78 for this series of adducts, suggesting that the unpaired electron is mainly localized on the cobalt atom.

EPR spectra of monomeric oxygen complexes. The EPR spectra of the oxygenated $\text{Co}(\text{sacac})_2\text{en}(\text{pyridine})$ in fluid and frozen toluene solutions are shown in Fig. 2 and the EPR parameters are tabulated in Table III. The oxygenated samples of the other bases give qualitatively identical spectra. These samples give the degassed spectra by exposure to nitrogen gas and the oxygenated spectra by exposing to oxygen gas again at low temperature. This indicates that the $\text{Co}(\text{sacac})_2\text{en}(\text{LB})$ reversibly reacts with molecular oxygen. The EPR spectra in the fluids split into eight lines due to a ^{59}Co nucleus, which give the implication of the formation of a monomeric complex, $\text{Co}(\text{sacac})_2\text{en}(\text{LB})(\text{O}_2)$. The spectra in frozen solutions split owing to a rhombic distortion, and then are complicated in perpendicular region. The g values and hyperfine constants were similar for this series of

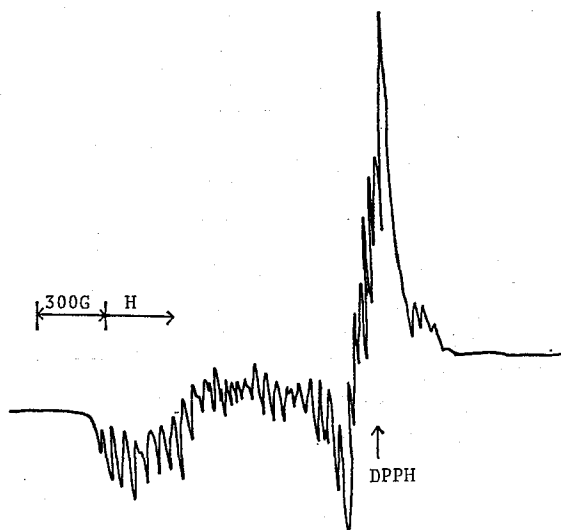


Fig. 3. EPR spectrum of $\text{Co}(\text{sacac})_2\text{en}$ in toluene- N,N -dimethylformamide solution at 77 K.

Co(sacac)₂en'(LB). This insensitivity to the axial ligand may imply that the axial ligand plays the role of elevating the Co d_{z²} orbital and assisting the electron transfer from Co atom to oxygen molecule, though it does not directly interact with unpaired electron of Co(sacac)₂en(LB) (O₂).

The degassed spectrum of Co(sacac)₂en in frozen N,N-dimethylformamide-toluene solution is quite different from the other spectra (Fig. 3), while this sample exposed to oxygen gas gives qualitatively identical spectra with the other oxygenated complexes. The origin of the difference for the degassed spectra is being investigated at present.

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